

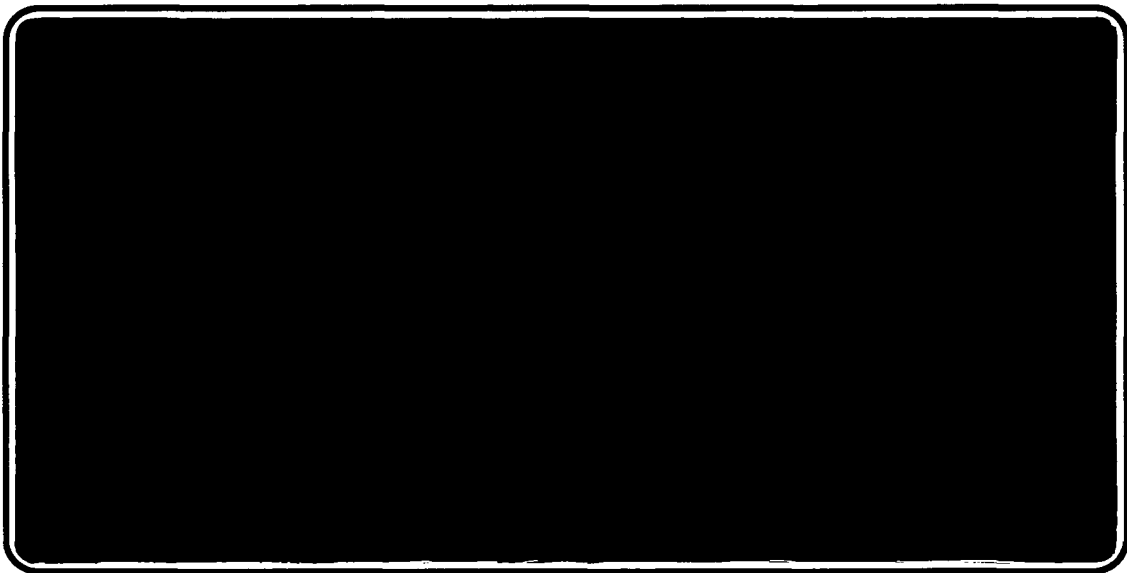


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**XYLOGLUCAN SORPTION ONTO CELLULOSE**

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## XYLOGLUCAN SORPTION ONTO CELLULOSE

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**ABSTRACT**

The sorption of xyloglucan from the seed of *Tamarindus indica* onto cellulose fibers was investigated. The high molecular weight polymer ( $1.4 \times 10^6$ ) exhibited monolayer adsorption on the cotton linters. The results are compared with earlier work on the sorption of xyloglucan fragments and are discussed in terms of polymer adsorption theory.

**INTRODUCTION**

Xyloglucan<sup>3</sup> is a hemicellulose found in the primary cell walls of many plant species. Found adjacent to the cellulose (CL), it is believed to function as a cementing material which contributes both crosslinks and rigidity to the cellulose framework. The only noncovalent linkage reported (8) in the primary cell wall cellulose-hemicellulose-pectic polysaccharide matrix of *Acer pseudoplatanus* cultured tissues is that between XG and CL. Therefore, the XG: CL association has been of great interest to researchers.

XG can be bound to CL *in vitro* to simulate this *in vivo* relationship. Previously, the sorption of <sup>14</sup>C labeled XG fragments onto CL under non-physiological conditions had been studied by Valent and Albersheim (14). Using seven- and nine-sugar XG fragments, they found that the addition of organic solvents (acetone or ethanol) was necessary to promote adsorption. They examined the effect of two variables (temperature and pH) on the

sorption of these fragments onto CL. A decrease (~20%) in the amount of XG adsorbed was reported with increasing temperatures (2° C to 45° C). Varying the apparent pH of the solution between pH 2 to 7 did not affect the binding of XG onto CL.

Hayashi, Marsden, and Delmer (5), examined aqueous XG-CL interactions *in vitro* using a radioiodinated pea XG. From their sorption experiments, they concluded that monolayer sorption occurred and approximated the maximum equilibrium amount at 5 micrograms of pea XG adsorbed per 100 micrograms of pea CL. Above pH 6, they demonstrated that sorption of XG onto CL was inhibited. The adsorption onto CL was found to be very specific and not affected by the presence of other  $\beta$ -glucans.

The present study examined the sorption of an unlabeled XG polymer isolated from *Tamarindus indica* onto CL fibers (cotton linters) in an aqueous environment. The amount of XG adsorbed was measured indirectly by analyzing the change in supernatant XG concentration. Thus, a seed wall XG was utilized to examine the sorption of XG onto CL fibers without labeling or significantly altering the natural polymer.

## MATERIALS AND METHODS

Kooiman's procedure (11) for isolation of XG from ground *T. indica* seed powder was modified. Ten grams of decorticated, benzene-extracted, ground *T. indica* seed powder was dispersed in a small amount of distilled water (30-50 mL) prior to extraction for one-half hour in boiling, distilled water (1 L). The suspension was filtered through coarse grade filter paper in a buchner funnel and then through a layer of diatomaceous earth (Manville) in a medium grade fritted glass filter funnel. To the stirred filtrate 600 mL of 96% ethanol was added and the gelatinous precipitate was drained on cheesecloth and squeezed out to remove as much alcoholic liquid as possible. The fibrous mass was stirred with 50% ethanol (100 mL) and the liquid was squeezed out. Purification of this crude XG per Kooiman's method with Fehling's solution was unnecessary since no associated proteins were detected. The sample was then concentrated *in vacuo* to remove ethanol and then freeze dried. A yield of approximately 33% was obtained.

Complete characterization of the isolated XG will be presented elsewhere. XG sugar and methylation analysis gave results similar to those seen in the literature (9,11). No significant amounts of any acetyl, pyruvate, or carboxyl groups were found on the XG isolated for this study. Size

exclusion chromatography was used for determining the XG's molecular weight distribution. A peak value molecular weight of  $1.4 \times 10^6$  was obtained. This value is much higher than those (9,10) reported in the literature and is either due to the milder isolation procedure followed here or to the different methods employed for measuring the molecular weights.

Cotton linters were obtained from Alpha Cellulose Corporation. These linters were extracted to remove any residual oils or extractives and then were solvent exchanged (12) to produce a pulp that was easily dispersable when shaken with water. Constant rate filtration resistance measurements (6) of the cotton linters were used to determine hydrodynamic specific surface area (area exposed to fluid drag;  $1.06 \text{ m}^2/\text{g}$ ).

Cotton linters of a known moisture content and distilled water (pH 5.8) were weighed directly into 50 mL polycarbonate centrifuge tubes with screw caps. After sealing, the tubes were shaken to disperse the linters and placed on an agitator in a constant temperature bath ( $25.0 \pm 0.5^\circ \text{C}$ ) along with the XG stock solution. The next day, the tubes and the stock solution were removed from the bath and a predetermined amount of XG stock solution was weighed into each tube. The tubes were sealed and returned to the agitator for a set length of time. The tubes were then removed and the supernatant was rapidly isolated through coarse fritted glass filter funnels. The filtrate was analyzed for XG concentration using Kooiman's iodine/potassium iodide procedure (10). Sorption of XG was calculated from the difference between its initial concentration and that in the filtered supernatant.

## RESULTS

XG sorption onto CL fibers at  $25^\circ \text{C}$  was followed with respect to time. At approximately 24 hours, a plateau was reached indicating that equilibrium had been attained. This time was much longer than in the pea XG sorption experiments reported by Hayashi, *et al.*, (5) in which equilibrium was attained within 4 hours at  $40^\circ \text{C}$ . This difference could be due to the larger molecular weight ( $1.4 \times 10^6$  vs  $3.3 \times 10^5$ ) and lower temperature ( $25^\circ \text{C}$  vs  $40^\circ \text{C}$ ) used in the present work or to different concentrations of XG and CL surface. Subsequent experiments were run 48 hours to guarantee equilibrium sorption.

The effect of XG concentration on sorption was next examined. All sorption

experiments indicated a rather rapid increase in specific sorption ( $\Gamma$ , mg XG/g CL) with increasing equilibrium (i.e., unadsorbed) XG concentration ( $C_e$ ). This was followed by a plateau region at higher  $C_e$  values suggesting monolayer adsorption. Figure 1 shows the adsorption isotherm for one run. The data can be fit to the Langmuir adsorption isotherm (1).

$$\Gamma = \Gamma_m K C_e / (1 + K C_e) \quad (1)$$

where  $\Gamma_m$  is the maximum specific adsorption (monolayer coverage) in the plateau region and  $K$  is the Langmuir affinity constant. The values for the data in Figure 1 are 4.0 mg/g and 143 mL/mg, respectively. The curve shown in Figure 1 was calculated using these values. The scatter at large values of  $C_e$  is the result of taking the difference between two large numbers (initial and equilibrium concentrations of XG) to obtain the amount adsorbed. The average value from eight experimental adsorption isotherms was 4.1 mg XG adsorbed/g CL with a standard deviation of 0.3 mg/g.

## DISCUSSION

The specific sorption found here may be compared with that of other polymers that have been sorbed onto CL fibers (Table I). The specific sorption is similar for the various materials, even when the polymer/surface interaction is primarily ionic (cationized polyacrylamide) rather than hydrogen bonding. The substrate used by Hayashi and co-workers (5) was prepared by grinding cotton fibers under liquid nitrogen. The specific surface area would depend on the resulting particle size and would likely be larger than 1 m<sup>2</sup>/g. This would account for the larger specific sorption found by these workers.

It is difficult to compare Valent and Albersheim's (14) XG sorption study to the processes that take place in the primary cell wall of plants and to the present results. The use of non-physiological conditions (i.e., organic solvents), XG fragments (rather than the intact polymer), and labeling of the XG fragments could significantly alter the adsorption properties of this hemicellulose.

The failure of XG fragments to bind to CL in water suggested to Valent and Albersheim (14) that the XG chain lifts off the CL surface and initiates XG chain creep. An alternative interpretation of this phenomenon can be presented using accepted polymer adsorption theory. For any solute,

adsorption occurs when the free energy of the adsorbed molecule is less than that for the same molecule in the surrounding solution. For oligomers, solubility increases as molecule weight decreases (3). Thus it is to be expected that XG fragments would have a high solubility in a good solvent (water) and a corresponding low potential for adsorption onto a surface. The converse (reduced solubility and ready sorption) would be expected for a high molecular weight XG. Thus the lack of sorption from water of XG fragments is a matter of solubility and is not relevant to the postulated mechanism of XG chain creep. Additional work to be reported elsewhere has shown that  $\Gamma_m$  for XG on CL is independent of molecular weight in the range  $2 \times 10^5$  to  $1.9 \times 10^6$ .

The time-averaged fraction of segments of a XG chain that are bound to the CL surface depends on the polymer-solvent interaction parameter and the polymer-surface interaction parameter (3). Strong polymer adsorption (such as found in this work) does not disallow the inch-worm-like detachment and reattachment of a chain (8), because the state of a given polymer segment is in dynamic equilibrium. Whether a given segment is adsorbed at a particular moment depends on its thermodynamic interactions with the surface and the surrounding aqueous solution and also on any external mechanical stresses on the chain. The latter might result from the elongation of the cell wall to which the XG was attached. Thus the state of a given XG segment *in vivo* might be described by the following scenario: a) adsorption onto the cell wall, b) desorption mediated by the mechanical stress caused by cell wall growth, and c) readsorption at a new site on the cell wall displaced from the first by the amount of cell wall elongation.

Albersheim and co-workers (8) hypothesized that the CL fibrils were covered by a XG monolayer in the primary cell wall. The plant cell wall model of Chambat, Barnoud, and Joseleau (2) postulated XG to XG linkages or multilayers of XG. The *in vitro* XG experiments of Hayashi, et al., (4,5) and of this work have found only monolayer sorption.

## ACKNOWLEDGEMENTS

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**FOOTNOTES**

<sup>3</sup> Abbreviations: CL, cellulose; XG, xyloglucan

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**Table II.** *Sorption of Water Soluble Polymers onto CL Fibers*

Polymer	Molecular Weight	$\Gamma_m$	CL	Specific surface area	Ref.
		<i>mg/g</i>		<i>m<sup>2</sup>/g</i>	
XG	$1.4 \times 10^6$	4.1	c	1.06	This work
XG	$3.3 \times 10^5$	14 <sup>b</sup>	d		(5)
Polygalactomannan	a	3	e	0.99	(7)
Cationized polyacrylamide	$2.7 \times 10^6$	8	f	1.04	(13)

<sup>a</sup>Intrinsic viscosity of 13.4 dL/g in deionized water at 25°C. <sup>b</sup>Single point, presumably in plateau region. <sup>c</sup>Cotton linters. <sup>d</sup>Ground cotton fiber. <sup>e</sup>Bleached kraft pine fibers. <sup>f</sup>Oxidized cotton linters.

Figure Caption:

**Figure 1.** Equilibrium sorption of XG on CL as a function of unadsorbed XG concentration. Curve is a Langmuir fit to the data.

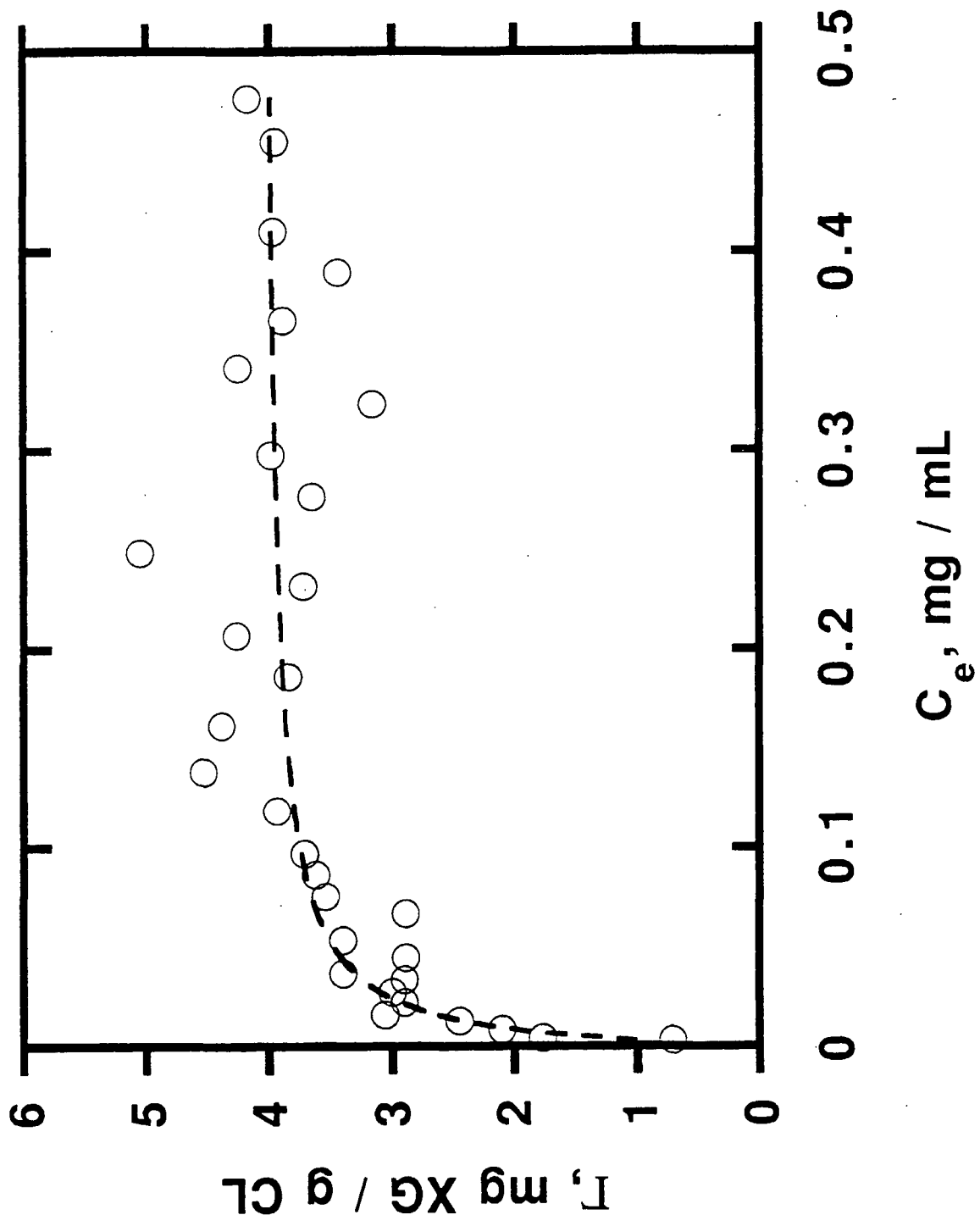


Figure 1.